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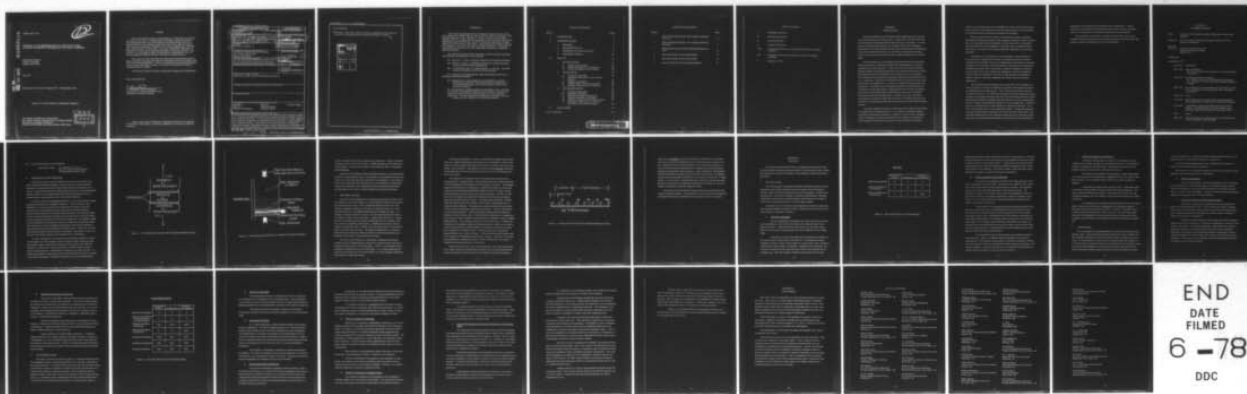
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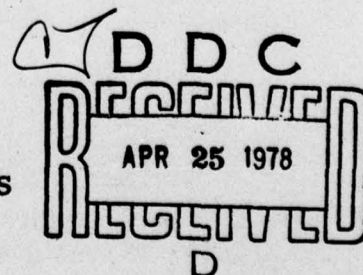
University of Dayton
Research Institute
Dayton, Ohio 45469

July 1977

Final Report for Period 15 August 1976 - 30 September 1976

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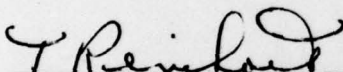
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This technical report has been reviewed and is approved for publication.

FOR THE DIRECTOR



T. REINHART, Project Engineer
Composites & Fibrous Materials Branch
Nonmetallic Materials Division

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Advanced Composites	Titanium-Epoxy											
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)												
<p>A three-dimensional interphase exists at the boundary between polymer (adhesive or matrix) and substrate (adherend or reinforcing fiber) in adhesive joints and composite materials. To fully understand the significance of this region on the mechanical properties and durability of these materials, an interdisciplinary workshop was held. The results of that workshop were to identify the known and unknown relationship between interphase parameters and mechanical, thermal and chemical durability of adhesive joints and advanced composite (over)</p>												

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materials. This report serves as both an assessment of the state-of-the-art of the interphase and a consensus for future research.

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FOREWORD

This report was prepared by the University of Dayton Research Institute, Dayton, Ohio 45469 under Air Force Contract F33615-76-M-5452. The principal organizer is Dr. Lawrence T. Drzal. The Air Force Project Monitor is Mr. T. Reinhart of the Composites and Fibrous Materials Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433. This workshop was funded under the joint auspices of the Air Force Office of Scientific Research, Directorate of Chemical Sciences and the Air Force Materials Laboratory; Nonmetallic Materials Division.

The following personnel of the University of Dayton Research Institute participated in the operation of this workshop:

Dr. Lawrence T. Drzal - principal organizer and workshop chairman

Mr. Robert L. Conner - coordinator of Research Institute personnel involved in the workshop management

Mr. J. Holverstott, Mrs. P. Collins and Ms. J. Mescher - provided technical assistance with the workshop operation

It is a pleasure to acknowledge the large contributions made by the following workshop participants:

Dr. Armand Lewis, Lord Corporation - provided the conceptual framework around which the multidisciplinary discussions of the workshop took place, and for his valuable critique of the workshop summary

Dr. George Hardy, Celanese Research Corporation; Prof. John Manson, Director of Materials Research Center, Polymer Laboratory at Lehigh University; and Dr. William Jones, Air Force Materials Laboratory - for their assistance in leading the workshop discussion groups and their critique of the workshop summary

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LIST OF SYMBOLS

N	Negligible interaction
M	Moderate interaction
S	Strong interaction
U	Unknown interaction
U(M)	Unknown interaction but probably moderate based on group consensus
U(S)	Unknown interaction but probably strong based on group consensus
Å	Angstrom 10^{-8} cm

SECTION I

INTRODUCTION

The use of adhesives in aircraft structural applications is increasing in both the military and civilian sectors. Studies have indicated that adhesive bonding offers significant weight reductions and cost savings. Cost savings can be achieved through the use of simpler fabrication techniques, improvement in structure fatigue life and reduced operating and maintenance costs while weight reduction can be achieved by incorporation of designs using reduced stress levels which result in improved fatigue life of components.

At the present time, costly engineering development and verification testing programs are usually associated with implementation of adhesive technology to aircraft structure. These efforts are directed primarily at defining suitable manufacturing processes and controls necessary to provide high initial adhesion and durability of the "bondline" in the environment. Such programs rarely generate fundamental information about adhesion and, as a consequence, repetition of substantial portions of these efforts are necessary when new materials (i. e., adhesive or adherend) and processes are introduced. In addition, the environmental durability of bonded joints are evaluated by accelerated testing. Interpretation of the results (for application to service life prediction) is difficult because the basic degradation mechanisms have not been determined. Further, the costly simulated environment verification testing will continue to be required unless the fundamental requirements for adhesion and curability are understood and implemented.

Currently, adhesion research is being directed at improving the material properties of the adhesive per se, e. g. relation of moisture sorption properties of adhesives to structure. However, because of the complexity of the "interphase" formed at the juncture of the adhesive and adherend, only fragmented efforts exist to define the region of polymer substrate

contact on a molecular level, and to identify the surface and material parameters of adhesive and adherend (or fiber and matrix) that are most important to initial high adhesion and long term interfacial durability.

Because of the Air Force desire to incorporate advanced composite and adhesive bonding technology in future weapons systems in order to realize their cost and weight saving advantages, the Air Force Office of Scientific Research and the Air Force Materials Laboratory have co-sponsored this workshop on "The Role of the Polymer-Substrate 'Interphase' in Structural Adhesion".

The purpose of the workshop is to bring together representatives of the government, industrial and academic communities from the scientific and engineering disciplines that are an integral part of the polymer-substrate interphase for the purpose of determining first, what has been scientifically established about the role of the polymer-substrate interphase in adhesion and, secondly, what areas remain to be addressed so that the 'interphase' is not or does not become the "weak link" in the strength or durability of adhesive bonds or advanced composites for long life aircraft structural applications.

This workshop is the beginning of a process which will eventually provide the direction in which to marshall our scientific and engineering efforts to eventually arrive at that answer. This is the critical moment in history to conduct this effort. In a world now recognized as having limited resources, advances in materials technology and hence societal advancement will become increasingly dependent on designs which incorporate a variety of materials to produce a system with optimum properties for a given application. Adhesion has to be an integral part of those designs for combining materials. Likewise, scientifically this is a most opportune moment. Recent developments in surface spectroscopic techniques now for the first time allow atomic and molecular identification of the outermost surface layers of materials so that molecular interactions between polymer and substrate can be identified and

degradation mechanisms at the interphase can be understood. Fracture mechanics is progressing to the point where the effect of layers only thousands of nanometers thick on mechanical properties can be analyzed.

This workshop, through the conclusions summarized in this report, hopefully will provide the direction for future research so that the role of the polymer-substrate interphase can be truly understood.

SECTION II
WORKSHOP AGENDA

Title: The Role of the Polymer-Substrate 'Interphase' in Structural Adhesion

Sponsors: Air Force Office of Scientific Research and the Air Force Materials Laboratory

Date and Location: September 9th and 10th, 1976
Bergamo Conference Center
Dayton, Ohio

SCHEDULE:

9 September 1976

0700-0815	Registration
0815-0830	Opening Remarks - Dr. Frank Kelley, Chief Scientist, Air Force Materials Laboratory
0830-0900	Workshop Introductory Remarks - Dr. William Jones, Air Force Materials Laboratory - Dr. Lawrence T. Drzal, University of Dayton Research Institute
0900-1200	Presentations from representatives of government, industry and academia on various aspects of the 'interphase' as we know it
1200-1300	Lunch
1300-1330	Presentation by Dr. Armand Lewis on the Interaction Matrix Approach to be used in the workshop discussions
1330-1700	Formulation of Interaction Matrices by each of three groups: Fracture Mechanics, Polymer Physics and Rheology, and Surface Chemistry and Surface Physics
1830	Dinner
1900-1945	Presentation by Dr. Armand Lewis on "The Attachment Theory of Adhesive Joint Strength"

10 September 1976

0820-1030	Presentations of Interaction Matrix Findings to the entire audience by each group leader
1030-1200	Discussion and presentations from the participants
1200	Lunch and Adjournment

1. SPEAKERS

"Assessment of the Technological Capabilities of the Scientific Community in Relation to Air Force Future Needs"

Dr. Frank N. Kelley
Chief Scientist
Air Force Materials Laboratory
Wright-Patterson Air Force Base, Ohio

"Function of this 'Interphase' Workshop in Adhesion Research"

Dr. William B. Jones, Jr.
Air Force Materials Laboratory
Wright-Patterson Air Force Base, Ohio

"Goals and Organization of the Workshop"

Dr. Lawrence T. Drzal
Workshop Organizer and Chairman
University of Dayton Research Institute
Dayton, Ohio

"Chemistry of Epoxy Adhesives and Matrices"

Mr. Clayton May
Lockheed Missile and Space Company
California

"Surface Composition of Aluminum and Titanium Surfaces"

Mr. William Baun
Air Force Materials Laboratory
Wright-Patterson Air Force Base, Ohio

"Surface of Graphite Reinforcing Fibers"

Dr. Lawrence T. Drzal
University of Dayton Research Institute
Dayton, Ohio

"Interfacial Mechanics of Composites"

Dr. Thomas Hahn
University of Dayton Research Institute
Dayton, Ohio

"Fracture Mechanics and the Interphase"

Dr. Wolfgang Knauss
Dept. of Aeronautical Engineering
California Institute of Technology

"Graphite-Epoxy Interface and Matrix Properties"

Dr. Lewis Maus
Tulsa Division
Rockwell International
Tulsa, Oklahoma

"The Interaction Matrix and Its Use as a Workshop Discussion Format"

"The Attachment Theory of Adhesive Joint Strength"

Dr. Armand Lewis
Lord Corporation
Erie, Pennsylvania

2. DISCUSSION GROUPS

I. Surface Chemistry and Surface Physics of the Polymer-Substrate Interphase

Discussion Leader: Dr. George Hardy
Celanese Research Co.
Summit, N. J.

II. Polymer Physics and Rheology of the Interphase

Discussion Leader: Dr. John Manson
Lehigh University
Bethlehem, Pa.

III. Fracture Mechanics of the Interphase

Discussion Leader: Dr. William B. Jones, Jr.
Air Force Materials Laboratory
Wright-Patterson AFB, Ohio

3. DEFINITION OF THE INTERFACE

The juncture that occurs in an adhesive bond or in an advanced composite where the polymeric adhesive or matrix comes in contact with the adherend or reinforcement is the region about which this workshop is concerned. This juncture has until recently been described as a two-dimensional interface (Figure 1) or boundary layer which has functioned primarily to transmit stress continuously across it to its adjacent phases.

In reality, that two-dimensional interface is a three-dimensional region properly described as an interphase (Figure 2). The boundaries of this interphase are from some point in the bulk adhesive (matrix) where the microscopic local properties begin to change from the bulk properties, toward and through the actual boundary between adhesive and adherend where contact is made and into the bulk adherend (reinforcement) to the point where the local properties approach those of the bulk adherend. The dynamic model of this interphase also includes the thermal, mechanical and chemical fluxes which may traverse this interphase through either the adhesive (matrix) or adherend (reinforcement) or along the interphase itself. (Chemical, thermal and mechanical fluxes mean the limits of humidity, temperature, stress, etc. which are the design criteria for the adhesive joint or composite.)

A closer examination of this model of the interphase applied to current or anticipated Air Force systems such as aluminum-epoxy, titanium-epoxy and graphite-epoxy reveals that the polymer surface layer of the adhesive (matrix) is contained in a region on the order of 1000\AA in depth in which chemical heterogeneities, morphological variations and voids can exist. In between this polymer surface layer and the adherend surface layer is a region of molecular dimensions $\sim 100\text{\AA}$ where parameters such as adsorbed gases,

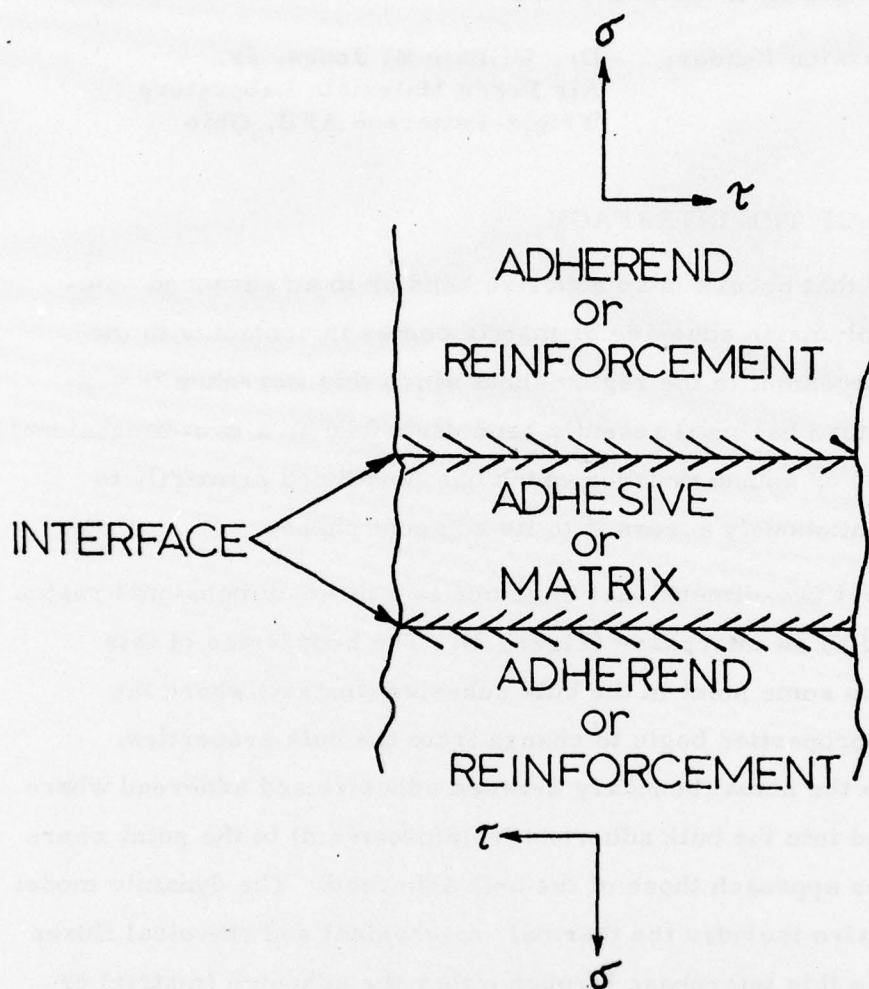


Figure 1. Two-Dimensional Concept of the Polymer-Substrate Juncture.

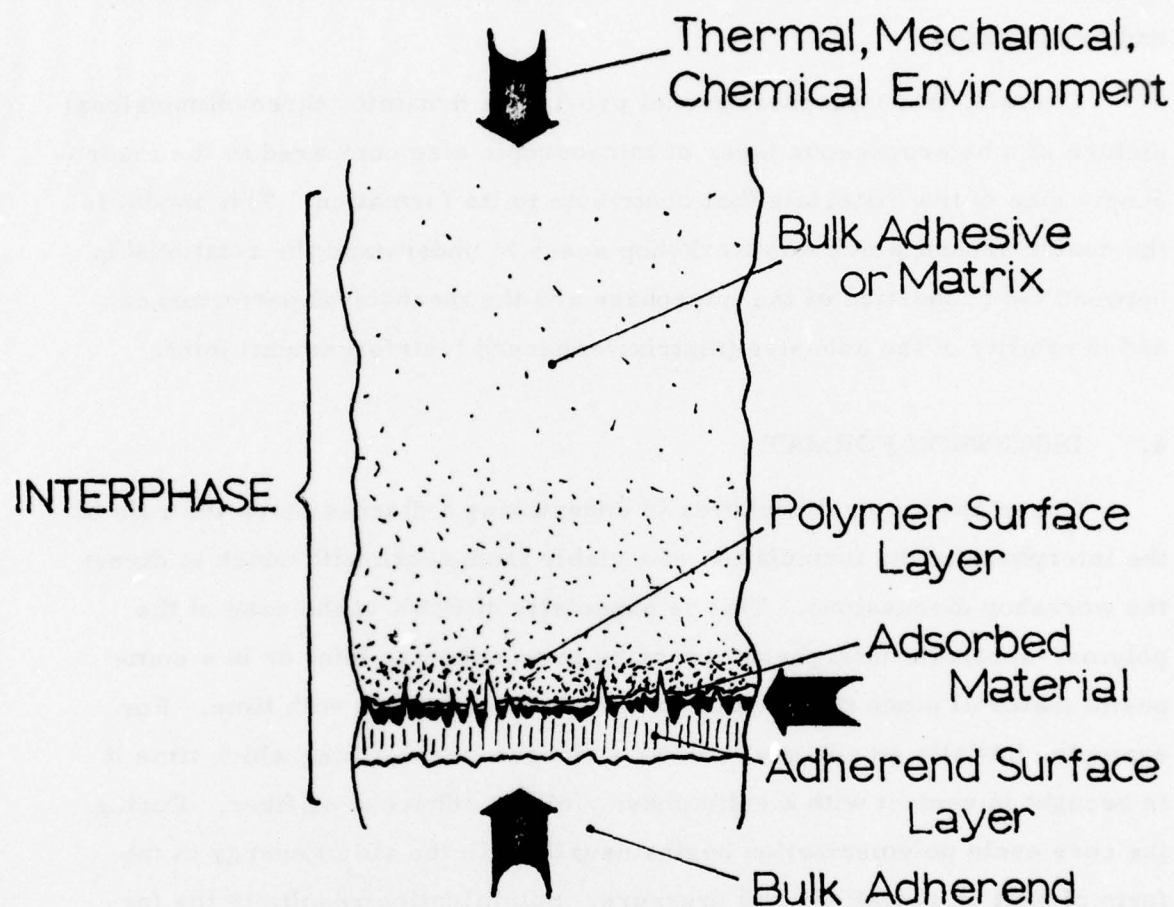


Figure 2. Three-Dimensional Model of the Polymer-Substrate Interphase.

surface chemistry and surface geometry are important. Finally, the adherend surface layer can be on the order of 5000\AA depending on the adherend or reinforcement. Included in this layer is the protective oxide, its porosity and morphology.

Overall, this interphase model provides a dynamic, three-dimensional picture of a heterogeneous layer of microscopic size compared to the macroscopic size of the materials that contribute to its formation. This model is the center around which this workshop seeks to understand the relationship between the properties of the interphase and the mechanical performance and durability of the adhesive (matrix)/adherend (reinforcement) joint.

4. DISCUSSION FORMAT

One of the major difficulties in undertaking a discussion on the role of the interphase is the formulation of a viable framework with which to direct the workshop discussions. This is especially difficult in the case of the polymer-substrate interphase occurring in an adhesive joint or in a composite material since the polymer physical state changes with time. For example, initially an adhesive can be a viscous liquid during which time it is brought in contact with a solid phase - either adherend or fiber. During the cure cycle polymerization begins usually with the aid of energy in the form of heat or radiation, and pressure. Solidification results in the formation of an adhesive joint. Finally, that joint must function in its environment for a finite period of time. Evaluation of parameters is, therefore, difficult because different conditions and hence different parameters predominate at each stage of bond formation or usage.

The other major difficulty in conducting a workshop of this nature results from the multidisciplinary nature of the subject and the spectrum of disciplines represented by the participants. Table 1 is a breakdown of participants by employment sector and discipline. It is readily apparent that differences in perspective of the participants can create language difficulties which hinder in-depth discussion.

With these complexities in mind, an approach was adopted which would allow for complete exploration of all aspects of the interphase, create a minimum of communicational difficulties and would be workable in the time limitations of the workshop. This approach involved setting artificial boundaries for the discussion and forming discussion groups from the workshop participants by discipline.

The details of this approach were formulated and presented to the workshop by Dr. Armand Lewis. The workshop discussion format consisted of first separating the participants into three major categories. Participants categorized themselves as being able to contribute the most in a discussion group concerned primarily with polymer physics and/or rheology, surface chemistry and/or surface physics or fracture mechanics. Second, the lifetime of the interphase was artificially subdivided for discussion purposes along the time axis into three stages. An initial stage termed the "wetting" stage described the first few minutes of time when a fluid polymer was in contact with the adherend. The primary occurrence during this time period was flow and thermodynamic wetting of the substrate. This was followed by a second stage termed the "curing" stage where polymerization within the polymer was the primary event. This involved the application of temperature and pressure cycles or whatever external means are applied to affect complete polymerization. This usually occurred over a period of hours. Finally, the remainder of the polymer-adherend lifetime was said to exist over the period of time during which the polymer-adherend interphase functioned as an integral component of an adhesive joint. This was termed the "functioning" stage and exists over a period of years. The time relationships between each of these stages are illustrated with the aid of Figure 3. Obviously, the scales and boundaries are qualitative at best and these distinctions were made to simplify workshop discussions in each group.

The discussion of each of the three groups over each of the interphase's three stages centered on identifying and subjectively assessing material and surface parameters and their impact on the polymer-substrate interphase

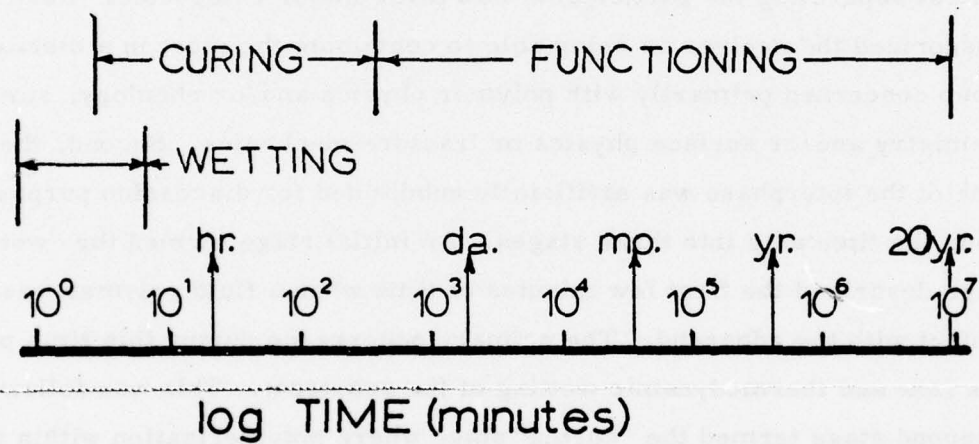


Figure 3. Relationship between Polymer-Substrate Stages and Time.

subjected to reasonable chemical, thermal and mechanical environments. This process involved establishment of an interaction matrix between surface, interfacial and material parameters with environmental factors in each of the time stages and qualitatively evaluating to the greatest degree possible the magnitude of the interaction. Since quantitative relationships between interphase parameters and environment rarely exist, a qualitative assessment was attempted and judged to be strong S, moderate M, or negligible N. In some cases, the participants were unable to cite any pertinent perspective and therefore judged that relationship as unknown U, but (e.g. Figure 4) projected an expected magnitude U(M).

The results of the workshop discussion groups were presented to the entire workshop assembly. The conclusions of each group incorporating the workshop discussion are presented in the results section of this report.

SECTION III

RESULTS

The results summarized here are a compilation of the efforts of the three workshop discussion groups presented in the interaction matrix format and separated according to the stages of the interphase lifetime previously discussed.

1. WETTING STAGE

The wetting stage of interphase formation includes that period of time during which the primary physical event occurring is the achievement of intimate contact between the adherend and the fluid polymer. At this developing junction, the surface energetics of polymer and adherend, adherend topography and interactions between polymer and adherend were judged to be the most important parameters of the interphase region.

A summary of the workshop on these parameters and their interaction with externally applied mechanical stress, temperature and chemical environment fluxes is displayed in Figure 4.

A. Adherend Topography

Surface preparations commonly used today increase the surface microroughness as well as affect the atomic and molecular state of the adherend surface. Neglecting for this discussion, any chemical surface effects, this increased rugacity alone can have an influence on the wetting stage.

Taking the case where the polymer and adherend are wettable in the sense that the contact angle is less than 90° , increasing the surface roughness will give a lower contact angle on a macroscopic scale, but microscopically the contact angle is unchanged. Roughness may contribute to an increase in surface area but may also lead to microvoid formation due to entrapped gas. Since the polymer systems discussed here are viscous,

WETTING

	Mechanical Stress	Temperature	Chemical Environment
Adherend Topography	M	N	N
Surface Energetics of the Adherend	N	M	S
Surface Energetics of the Polymer	N	S	U(M)

Figure 4. Interaction Matrix for the Wetting Stage.

additional mechanical stress would tend to aid this wetting process. However, the mechanical stress levels used in processing equipment would have at best a moderate effect on the wetting process. Temperature and chemical environment would not be expected to influence adherend topography in the context of the limits of this workshop. The surface oxides of these inorganic adherends would normally be unaffected by these environments.

B. Surface Energetics of the Adherend

A second factor intimately involved in the wetting process is the surface energetics of the adherend. This term can be defined as the surface free energy of the adherend using thermodynamic concepts. This quantity is a direct result of the molecular state of the adherend surface. The difference in surface free energy between adherend and polymer is the driving force for wetting. Adsorption of polymers, changes in polymer conformation, etc. are some of the observable phenomena that result from the surface free energy driving force.

The atomistic forces that give rise to the adherend surface energetics are unaffected by any normally applied external mechanical stress. The surface free energy decreases with temperature but over the limited temperature range under consideration here, this variation is moderate for these high melting solids. The strongest effect will be that of the chemical environment. For example, water molecules adsorbed on the surface can both mask the outermost adherend surface layer and/or react with the oxide to form a hydroxide layer. Both possibilities could strongly affect the energetics and ultimately the wetting process.

A combinational effect of these last two environments should be mentioned also. That is a coupling between temperature and chemical environment. The additional energy input can increase the speed of reaction of species with the surface or provide the activation energy for reaction, e.g. further oxidation. The inverse is also true. An additional energy input can initiate thermal desorption of species from the surface.

C. Surface Energetics of the Polymer

During the wetting stage, an additional consideration must be included in the surface energetics of the polymer because of the mobility of polymer components in this fluid state. Consideration must be given to polymer-polymer intra and inter molecular interactions.

Mechanical stress imposed on the adhesive system (neglecting very high pressure work) would have a negligible effect on the surface energetics because of the molecular nature of the forces involved within the polymer.

Temperature would have the strongest effect. Segmental mobility as well as chain mobility increases with increasing temperature. The rate of molecular diffusion of adhesive components will increase and concentration gradients due to the influence of the adherend surface are a likely possibility.

The imposition of a chemical environment would have an unknown effect. However, some reactive components of the adhesive could be adversely affected by the presence of water. Likewise, some polar intra or inter-molecular interactions could be reduced. The most reasonable estimate of the magnitude of this interaction between the adhesive surface energetics and the chemical environment during the wetting stage is moderate.

2. CURING STAGE

The curing stage is transitional between wetting and functioning of the adhesive joint. (The demarcation between wetting and curing is diffuse and this artificial separation has been made only to better organize the discussions. In actual practice curing can occur simultaneously with wetting.) It is characterized as being that period of time during which the primary events occurring at the interphase are reactions of molecular species with each other in the polymer phase (polymerization) and with the adherend surface

across the interphase. This period extends until the adhesive joint or composite becomes a load bearing component in a structure.

The most important parameters to be considered at this stage are listed in the interaction matrix of Figure 5.

The presence of an external mechanical stress was concluded as being negligible on all parameters in the curing stage.

A. Adherend Topography

As in the wetting stage, adherend topography refers to the physical characteristics of the adherend surface as distinct from the chemical. This is undoubtedly the least important parameter in this stage and exerts little or no effect on the interphase. Likewise, all the external environments applied exert negligible effect on this parameter.

B. Interphase Energetics of the Adherend Surface

During the curing stage, the adherend surface energetics can ~~affect cure in the interphase region.~~ This could occur through a catalytic effect of the adherend surface on the adhesive reactions or through adsorption of polymer components of the adhesive onto the surface resulting in localized variations in composition.

Mechanical stress during the curing stage would have negligible effect on the surface energetics. The effect of temperature, however, might be more substantial. Increasing temperature could provide the activation energy for specific reactions which would affect the surface energetics. Desorption of material or chemisorption of adhesive components could be enhanced changing the chemical state of the surface and thereby the surface energetics. The presence of an external chemical environment would have an unknown effect on this parameter.

CURING STAGE

	Mechanical Stress	Temperature	Chemical Environment
Adherend Topography	N	N	N
Interphase Energetics of Adherend Surface	N	M	U
Adhesive Composition	N	S	U
Adhesive Chemical Properties	N	S	N
Cure Rate/Conversion Adhesive Physical Properties Gas Solub	N	S	S

Figure 5. Interaction Matrix for the Curing Stage.

C. Polymer Composition

The components that constitute the major ingredients in an adhesive can be an important parameter in the interphase. Some may exhibit surface activity and adsorb at the adherend surface. Impurities, even at the parts per million level can have a profound effect on adhesive properties in the interphase. Curing agents like amines might be expected to have a different affinity for the adherend surface than the epoxy monomer. Low molecular weight material or unreacted components in the adhesive might tend to diffuse to the polymer-adherend boundary. The type and quantity of polar pendant groups on the epoxy monomer might also be expected to influence the interphase.

Temperature might be expected to have a strong effect on this parameter. Molecular diffusion would be enhanced allowing the influence of the surface chemical forces to be the limiting factor. The result would be to create variations in composition in the interphase. Chemical environment might be expected to have an effect on this parameter mostly through absorption of gases in the polymer or interaction with polymer components even impurities. The level of this interaction is unknown however.

D. Polymer Phase Chemical Properties

The chemical properties of the adhesive are intimately involved with the chemical composition and difficult to separate. For this discussion this parameter refers primarily to the cure rate and to the extent of conversion and crosslinking of the adhesive in the interphase.

The strongest interaction is between reaction rate and temperature. Epoxy systems follow Arrhenius relationships which propose an exponential dependence of reaction rate on temperature above the activation energy. In addition there exists a synergism between conversion of the reactants and the degree of crosslinking in the polymer network with temperature. An externally imposed chemical environment would be expected to have a negligible effect since the chemical properties are most strongly coupled to structure.

E. Polymer Phase Physical Properties

During the curing stage, many important physical properties of the adhesive must be considered as important. Discussion of these properties during the workshop was not sufficient to distinguish between different properties, so they were grouped together under this heading. For the curing stage, the important physical properties include the solubility of gases in the adhesive, volatility of the adhesive components, exothermic heat of reaction, and thermal conductivity.

When the solubility of desorbing gases in the adhesive is great enough, no bubbles are left at the adherend surface to act as points of stress concentration. Volatile reactants may act as gas generators during cure either at high temperature or low pressures.

Epoxy reactions are usually highly exothermic. If adiabatic heating takes place due to large masses of reacting materials, conversion, crosslinking, etc. can be strongly influenced which in turn would affect the functioning of the adhesive joint. It must be concluded that both the thermal and chemical environment can interact with the polymer physical properties quite strongly.

3. FUNCTIONING STAGE

The stage in the life of an adhesive joint or a composite material where the interphase becomes a load bearing member of a structure is defined as the functioning stage. This stage begins some time after the final processing of the adhesive joint or composite is complete and exists until the joint ultimately fails to fulfill its structural function. Both the adherend and the polymeric phase in this stage are solids and function in their design environment, i.e., within the stress, temperature and environment design limits. The results of the discussions on this stage are summarized in Figure 6.

FUNCTIONING STAGE

	Mechanical Stress	Temperature	Chemical Environment
Adherend Topography	M	N	N
Chemical Composition Network Structure Crosslink Density	S	S	S
Polymer Interphase Morphology	U(S)	U(M)	U(M)
Adherend Interphase Morphology	S	N	U(S)
Interphase Energetics	U(M)	U(S)	U(S)
Mechanical Properties	U(S)	U(S)	U(S)
Thermal Properties	U(S)	U(S)	U(S)

Figure 6. Interaction Matrix for the Functioning Stage.

A. Adherend Topography

The topographic character of the adherend must be considered as a parameter of an interphase in the functioning state. Macro roughness of the surface prevents interfacial failure from occurring along the polymer-adherend joinline due to interpenetration of polymer with adherend asperities.

This parameter itself is probably insensitive to any type of mechanical, thermal or chemical environment applied to it in the functioning stage.

B. Interphase Energetics

In the functioning stage, contact between polymer and substrate has been established. The type of bonding (physical vs. chemical) and the extent of each that takes place across the interphase has been established. This interaction is a necessary requirement for the transmittal of forces across the interface and for the functioning of the adhesive joint or composite as a structural entity both in the short term where good mechanical properties are important and in the long term where structural durability is paramount.

The response of interphase energetics to external environment is unknown. The effect of mechanical stress, thermal stimulus or chemical environment or any combination of these is unknown. Adequate experimental tools to investigate the interphase in situ are not available.

C. Adherend Interphase Morphology

In metal alloy adherends or graphite reinforcing fibers, adherend surface morphology is a variable that can affect interphase performance. Oxides formed as protective surfaces vary in thickness and structure and consequently mechanical properties with the process used to prepare them. Likewise, graphite fiber surface morphology depends to a great degree on the fiber processing conditions.

Actual data on the interaction of adherend surface morphology on the functioning of a joint is lacking; however, a strong relationship would be expected with an external mechanical environment because of the brittle nature of oxides similar to those found on these surfaces.

Temperature would have a negligible effect by itself on surface morphology but could be synergistic with chemical environment, e. g. hydration of aluminum oxides at elevated temperature causing a change in adherend surface morphology, or long term conversion of anatase to rutile.

D. Polymer Interphase Morphology

During the curing stage, morphological changes can occur in the polymer portion of the interphase that affect its behavior in the functioning stage. Currently, it is believed that epoxies generally form three dimensional branched networks of moderate molecular weight (agglomerates) which are dispersed in a matrix of material of lower molecular weight. The distribution of these agglomerates can be different in the interphase region than in the bulk. The distribution of these agglomerates within the interphase might be expected to influence the behavior of this region in the functioning stage.

Also included in this parameter would be the effect of voids and the presence and distribution of fillers, if present, in the polymer.

Once the morphology of the polymer in the interphase is determined, its response to external environment such as mechanical stress, temperature and chemical environment is unknown. However, any relationships are expected to at least be moderate at best.

E. Chemical Composition of Polymer Phase

The chemical composition of the polymer in the interphase is strongly related to the functioning of the bondline. The mechanical performance of the interphase will depend in large part on the network structure.

This parameter can be quantified by evaluation of features of the polymer such as the crosslink density, and molecular weight. The chemical composition also is responsible for the stability of this region in chemical environments, i.e. it is related to the susceptibility of specific bonds in the polymer to hydrolytic attack.

A mechanical stress environment alone would have negligible effect on the network structure and stability in the functioning stage. There would be a strong effect by an imposed thermal or chemical environment. The result of simultaneously or cyclically imposed mechanical, thermal and chemical environments must be considered also.

F. Mechanical Properties and Thermal Properties of the Polymer Phase

The interphase mechanical properties are difficult to distinguish from other parameters because ultimately they do depend on the composition and morphology of the materials in the interphase. However, they do represent a set of parameters on a different scale (i.e., continuum vs. molecular) which describe the behavior of the interphase region as it relates to the bulk mechanical properties of polymer and adherend and the functioning of the entire joint or composite in general.

Mechanical properties of the interphase necessary to characterize the contribution of the interphase to joint performance are quantities such as fracture toughness, shear modulus, Poisson's ratio and residual internal stresses. Transition temperatures, coefficient of thermal expansion and thermal conductivity of the interphase are some of the required thermal properties.

Relationships of these parameters to mechanical, chemical or thermal environments are unknown, but extrapolation from macro scale systems indicates that the interaction will be strong.

For completeness and maximum utility, some additional comments must be included with the summary of results of the workshop.

The phenomenon of wetting is perhaps the best understood stage of polymer-substrate interaction. Experimental techniques are available; the thermodynamics of the wetting process are understood; and investigations have been completed and are continuing in this area. The challenge in this area is to advance to the point where the molecular components of the surfaces involved are identified as to their role in the wetting process.

In general, the reaction mechanisms and kinetics of bulk polymerization are well understood. The conclusions reported here are extrapolated from bulk studies to the interphase. Unfortunately, trace components and small physical variations which could be justifiably neglected in bulk studies take on greater importance in this small interphase region. Future work to investigate these variations will have to be based on a realization of the increased influence exerted by minor constituents near the surface due to concentration variations caused by surface effects.

The least amount of information is available concerning the interphase in the functioning stage. This is due in part to the dichotomy of having fracture mechanics theories based on a continuum model of materials properties and an interphase region essentially molecular in dimension. The scale of the interphase in comparison to the composite or adhesive joint can be a factor of 10^4 smaller. An effort must be made to use fracture mechanics approaches that allow interphase effects to be analyzed for their part in joint or composite performance.

Coupled with this is a lack of experimental information about the interphase itself. Only recently has data become available that suggests the size of the region. Composition and mechanical properties can only be hypothesized as yet.

Mention must be made also of the aspects of the problem that were not adequately addressed. Because of time limitations and the qualitative nature of the results, the parameters listed are generic rather than specific. Many of these can be composed of an additional set of parameters. Future work will amplify these specifics. At this time, however, the entire scope of the interphase region is represented by these parameters.

Finally, the synergism between environments and the environmental history of the interphase has not been addressed but must be included as an integral part of this topic.

SECTION IV

CONCLUSIONS

The value of this workshop will have to be determined against the goals set for it. These were: to identify those relationships between interphase parameters and mechanical and durability performance which do exist; identify those issues which must be addressed to understand the role of the interphase in adhesion; and to foster the interdisciplinary approach and the communication necessary for fruitful research in this area.

If this workshop is viewed as the beginning of a process, it has been successful. Qualitative parametric identification and relationships with environments have been identified (Figures 4, 5, and 6). Future work will be directed at quantifying these parameters and relationships.

Interdisciplinary communication has begun and hopefully will continue in this area in the future.

The critical areas that need to be addressed have been identified. They are basically composed of three major parts. First, resources must be brought to bear to characterize the interphase in greater detail as to its composition, morphology and mechanical properties. Second, the elements of fracture mechanics must be applied to include an interphase region as part of an adhesive joint or composite to allow the interphase role in mechanical performance to be determined. Third, investigation at the molecular level must be coupled with the macro measurements used to characterize the interphase if the full potential of this region as an integral component of a structural adhesive joint is to be achieved.

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